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Sustainable fuels from renewable energy

Mogensen, Mogens Bjerg

Publication date:
2013

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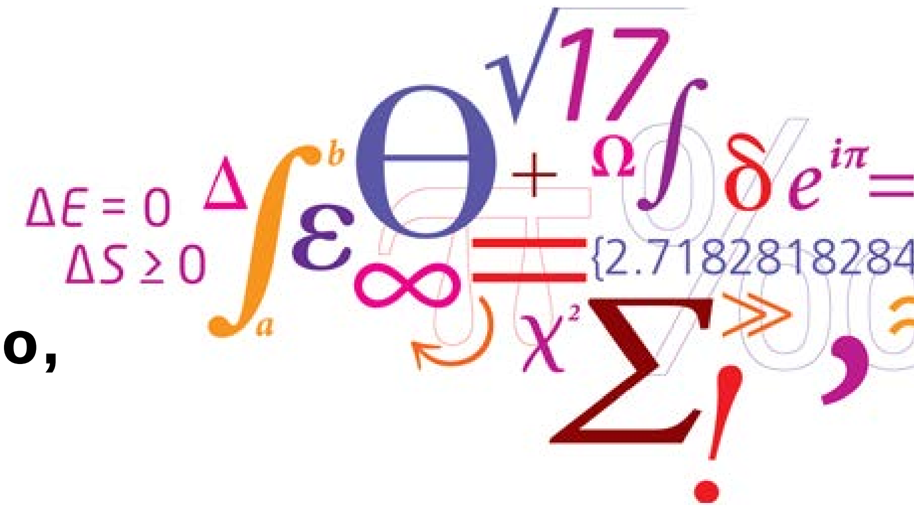
Acknowledgements to colleagues at DTU Energy Conversion

Mogens B. Mogensen



Talk at Politecnico di Torino, Italy May 21, 2013

DTU Energy Conversion
Department of Energy Conversion and Storage

Outline

1. Introduction – the climate issue, fossil fuel supply and what to do
2. Potential availability of renewable energy
3. Electrolysis is necessary
4. Synthetic fuels via syngas
5. Motivation for synthetic hydrocarbons
6. Vision
7. Thermodynamics
8. Types and status of electrolyzers
9. Economy
10. Concluding remarks

Introduction

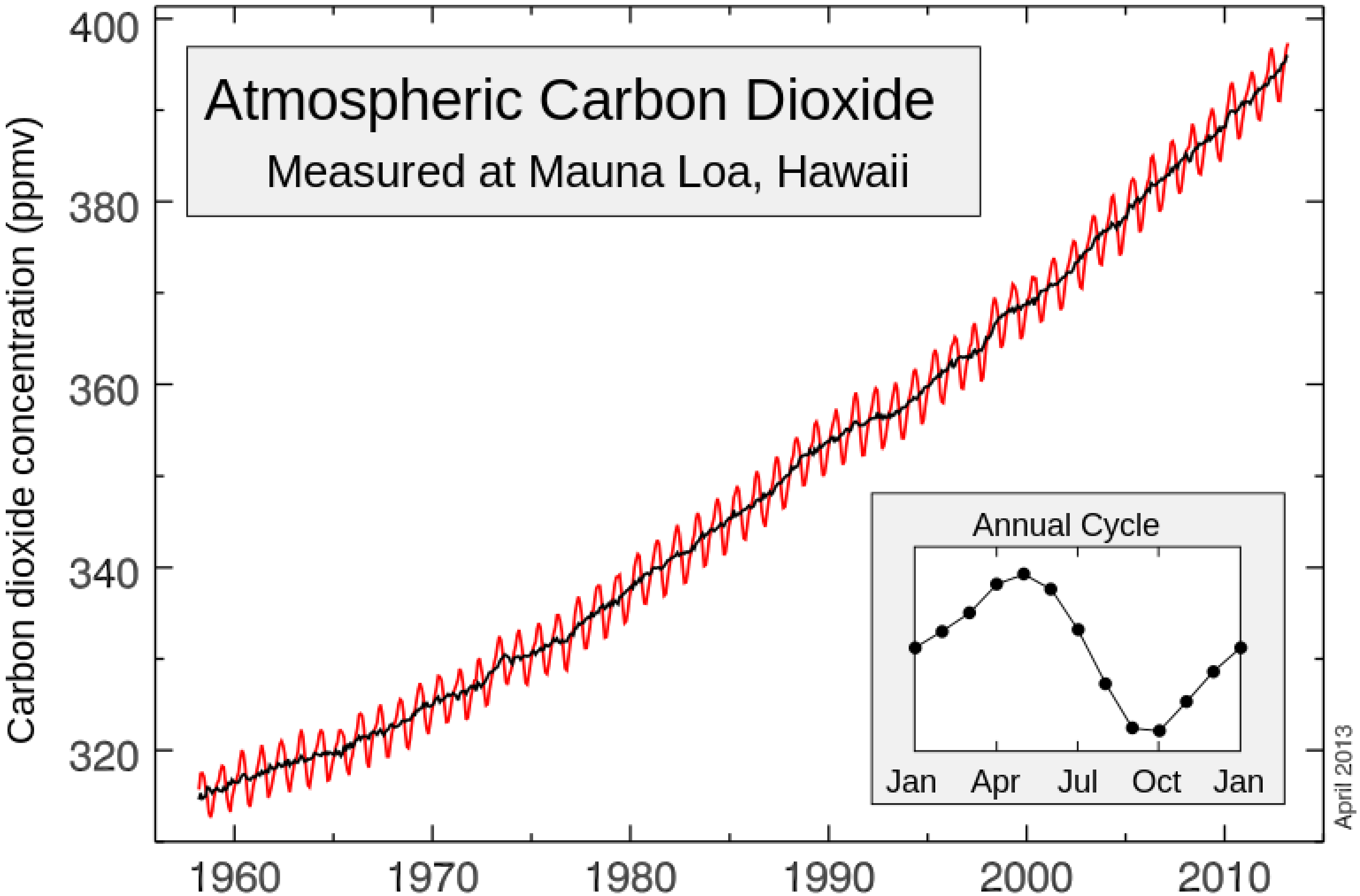
There are clear reasons to look for means of promoting fluctuating renewable energy:

- Probable anthropogenic climate change by CO_2 emissions
- Limited supply of cheap fossil fuel resources in the long term
- Security of supply and geopolitical consequences of unequal distribution of resources

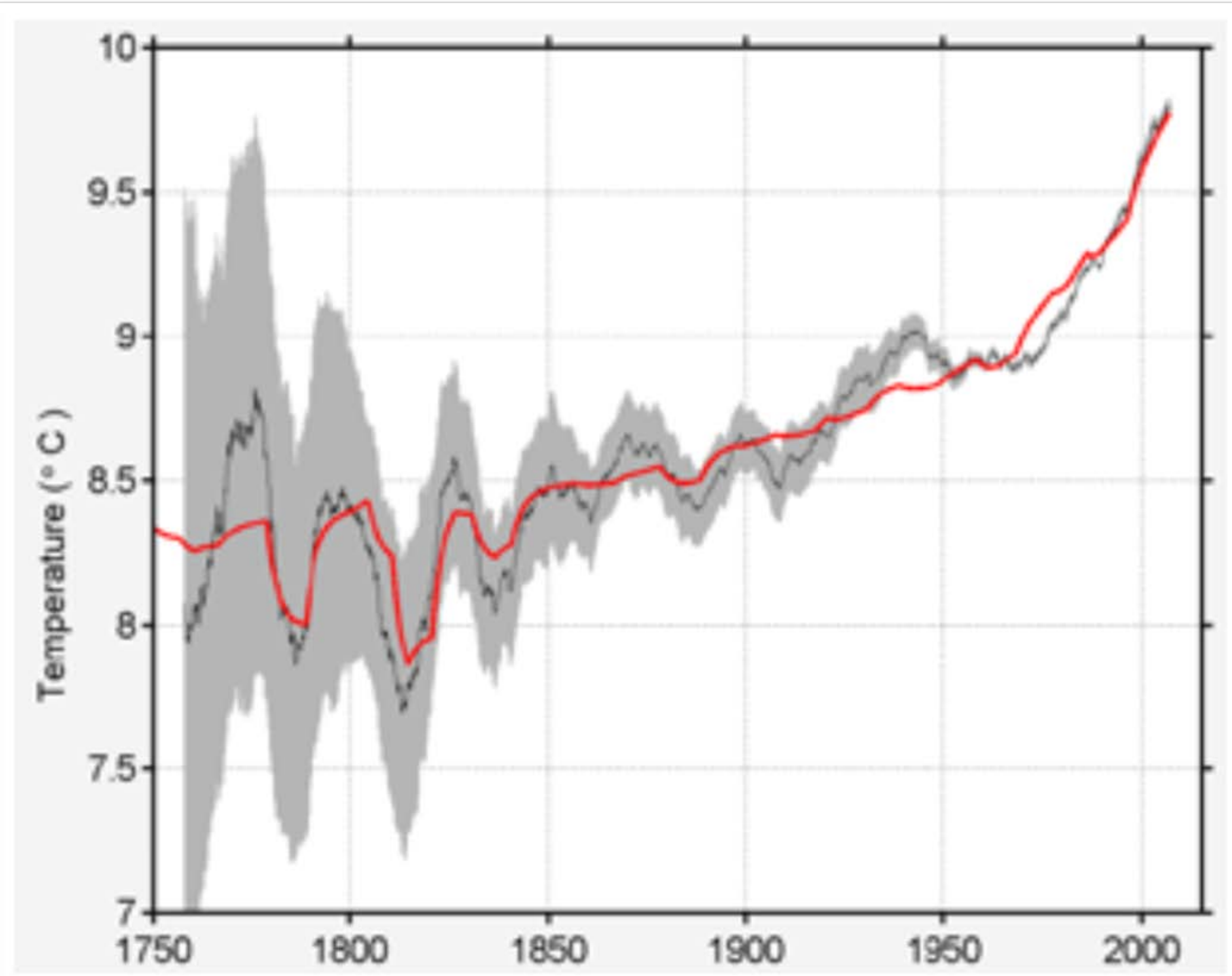
Synthetic fuels – CO_2 neutral green fuels - seem particularly benign to replace the fossil fuels.

This implies great perspectives of electrolysis and CO_2-recycling for production of sustainable and CO_2 neutral energy carriers.

Increasing CO2 concentration in the atmosphere



Anthropogenic climate change caused by CO_2 emissions?



Decadal land surface temperature from the BerkeleyEarth average (black line), compared to a linear combination of volcanic sulfate emissions (responsible for the short dips) and the natural logarithm of CO_2 (responsible for the gradual rise) shown in red.

From: *Rohde R, Muller RA, Jacobsen R, Muller E, Perlmutter S, et al. (2013) A New Estimate of the Average Earth Surface Land Temperature Spanning 1753 to 2011. Geoinfor Geostat: An Overview 1:1.*

What to do? – The Danish answer

- **Denmark aims to become independent of fossil fuel by 2050.**

  Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf

- **Natural to look for photosynthesis products (biomass), but not enough biomass**

  H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, http://www.concito.info/en/udgivelser.php

Enough renewable energy?

- **Yes, fortunately, enough is <u>potentially</u> available.**

- **The annual global influx from sun is ca. 3 - $4\cdot10^{24}$ J - marketed energy consumption is ca. $5\cdot10^{20}$ J;**

  References.:

  1)A. Evans et al., in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., p. 109.

  2) Earth's energy budget, Wikipedia, http://en.wikipedia.org/wiki/Earth's_energy_budget.

  3) International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, http://www.eia.gov/oiaf/ieo/index.html

- **Earth's surface receives at least ca. 6 - 8,000 times more energy than we need. In deserts, intensity is higher than average at the same latitude – dry air**

Area needed

- If 0.2 % of the earth's area (ca. 1 mill. km^2 or 15 % of Australia) and if collection efficiency = 10 %, we get enough energy.
- Actually less area is needed because:
- Besides solar we also have geothermal and nuclear (fusion and fission) potential energy sources.
- CO_2 free nuclear - more efficient if affordable storage technology is available.
- Important part of the solar energy is actually converted to biomass, hydro and wind energy – easier to harvest.

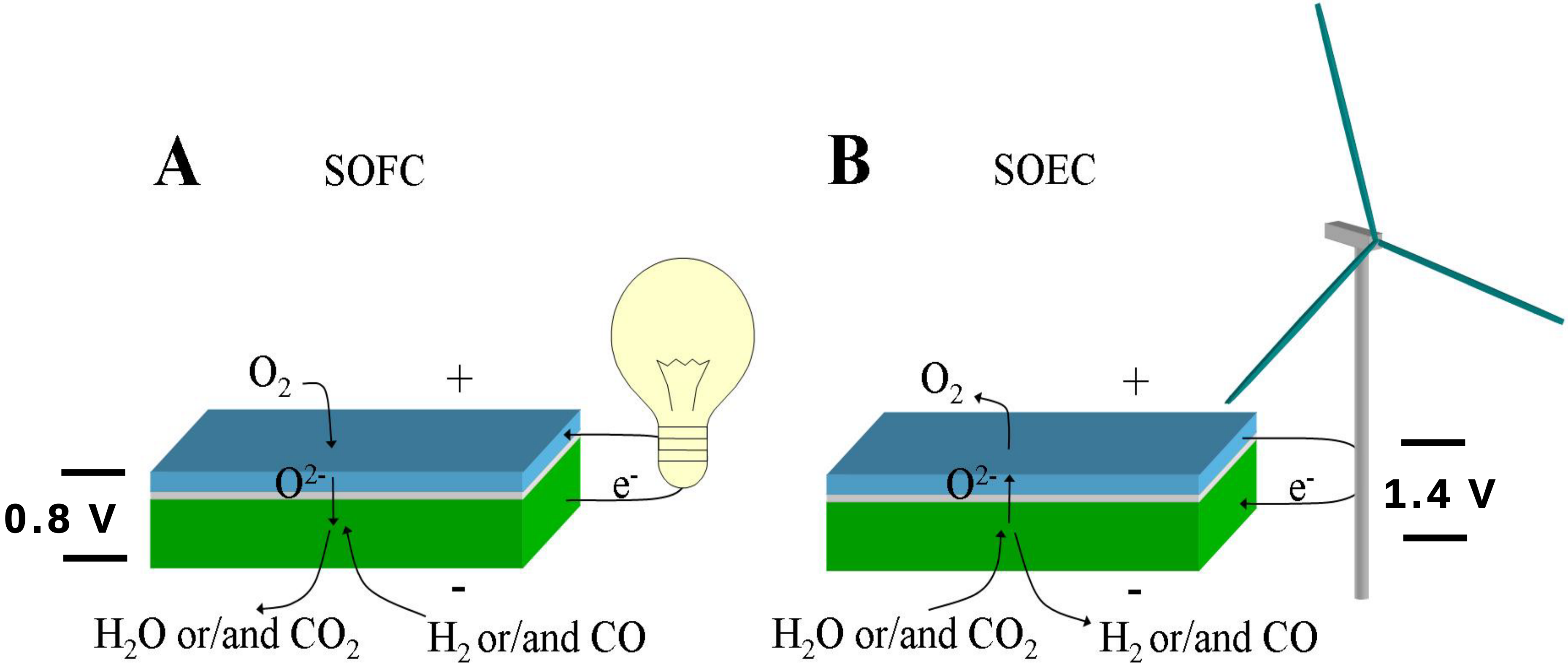
Electrolysis is needed

- Many technical principles are pointed out as suitable for storage technologies:
  - Pumping of water to high altitudes
  - Batteries
  - Superconductor coil (magnetic storage)
  - Flywheels
  - Electrolysis
  - Thermo-chemical looping
  - Solar Thermal Electrochemical
  - Photo-electrochemical HER and CO_2 reduction

- All are very important! But: first 4 are not for long distance (> 500 km) transport. 3 last are early stage research - may prove efficient in the future.

- Therefore, within a foreseeable future: Electrolysis is necessary in order to get enough renewable fuels!

Principle of electrolysis and fuel cell (SOC)



750 - 850 °C   EMF ca. 1.1 V

Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

Anode-supported SOFC

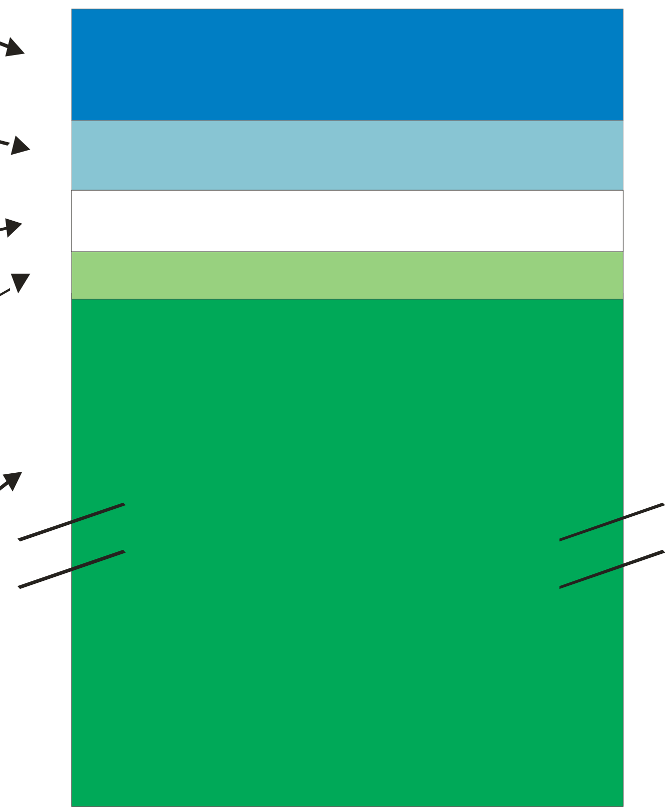
Cathode current collector, LSM, ~40 µm

Electrochemically active cathode layer, LSM/YSZ, ~20 µm

Electrolyte, YSZ, ~10 µm

Electrochemically active anode layer, Ni/YSZ, ~15 µm

Anode current collector (support), Ni/YSZ, ~330 µm

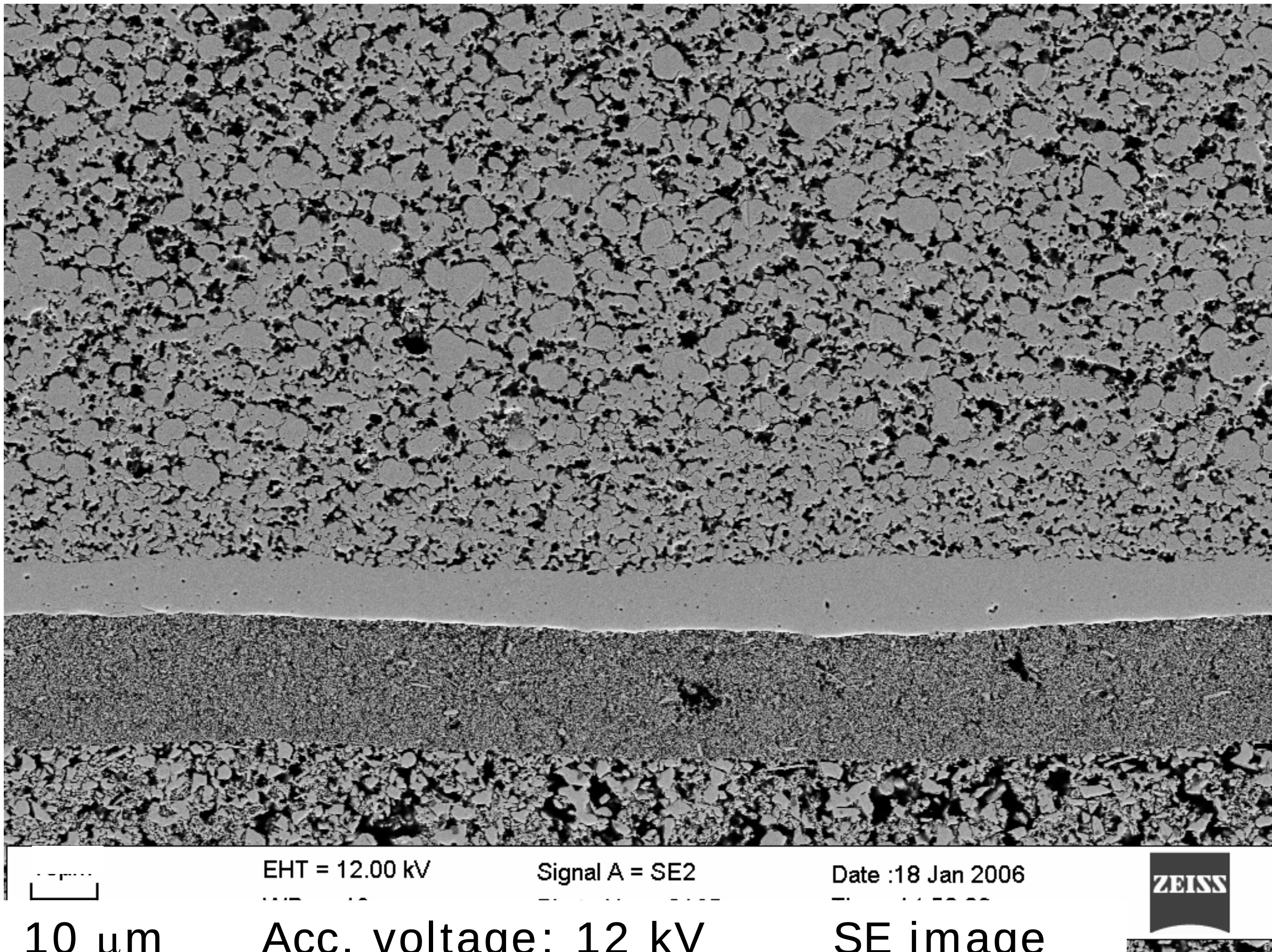


LSM = $(La_{075}Sr_{0.25})_{0.95}MnO_3$

YSZ = $Zr_{0.84}Y_{0.16}O_{1.92}$

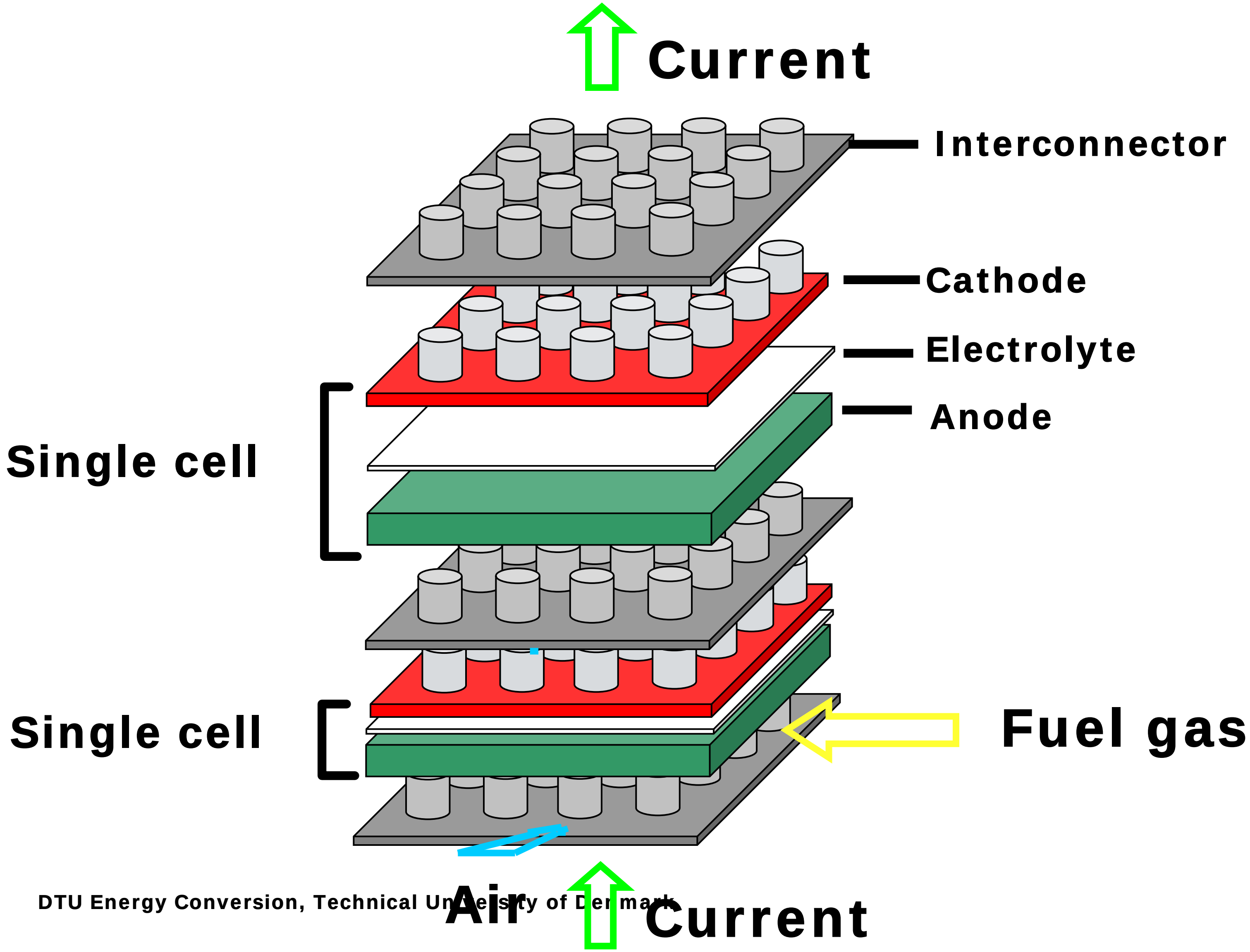
DTU Risø solid oxide cell

Ni-YSZ supported SOC



10 μm Acc. voltage: 12 kV SE image

Cell stack of many cell as ~1 V of each cell



Production of syngas (SOEC case)

Reaction Schemes:

The overall reaction for the electrolysis of steam plus CO_2 is:

$$H_2O + CO_2 + heat + electricity \rightarrow H_2 + CO + O_2 \qquad (1)$$

This is composed of three partial reactions. At the negative electrode:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad (2)$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (3)$$

and at the positive electrode:

$$2\ O^{2-} \rightarrow O_2 + 4e^- \qquad (4)$$

Production of syngas (from H_2 and CO_2)

The water-gas shift (WGS) reaction:

$$CO_2 + 2\ H_2 \leftrightarrows CO + H_2 + H_2O$$

By condensation of the water pure syngas is obtained

Methane synthesis

If H_2 only is produced by low temperature electrolysis:

- **$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ Sabatier reaction**

  or
- **make syngas from CO_2 by shift reaction and then:**

- **$CO + 3\ H_2 \leftrightarrows CH_4 + H_2O$**
- **Ni - based catalysts,**
- **190 °C – 450 °C**
- **3 MPa, i.e. pressurized**

- **in principle possible to produce inside SOEC stack on Ni-electrode, but CH_4 is not thermodynamical favored at 650 °C +**

Methanol and DME synthesis

- $CO + 2\ H_2 \leftrightarrows CH_3OH$
- $2\ CO + 4\ H_2 \leftrightarrows (CH_3)_2O + H_2O$
- A $Cu/ZnO\text{-}Al_2O_3$ catalyst
- 200 °C - 300 °C
- 4.5 - 6 MPa, again the electrolyzer should be pressurized

Liquid hydrocarbons
Fischer–Tropsch synthesis

- $(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$

- Various catalysts possible - most common are cobalt, iron, and ruthenium

- A mixture of hydrocarbons are formed – dependent on catalyst and operation conditions

- Kinetics increases with increasing pressure and temperature

- Possible temperature range 200 – 300 °C

Why synthetic hydrocarbons?
The energy density argument

Comparison of Energy Storage Types. Only the batteries are including containers.

Storage type	MJ/L	MJ/kg	Boiling point, °C
Gasoline	33	46	40 – 200
Dimethyl ether - DME	22	30	- 25
Liquid methane	24	56	-162
Liquid hydrogen	10	141	-253
Compressed air – 20 MPa	0.1	0.4	
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

Why synthetic fuel?
The power density argument

- Gasoline filling rate of 20 L/min equivalents <u>11 MW</u> of power and means it takes 2½ min to get 50 l = 1650 MJ on board

- For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.

- The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.

Visions for synfuels from electrolysis of steam and carbon dioxide

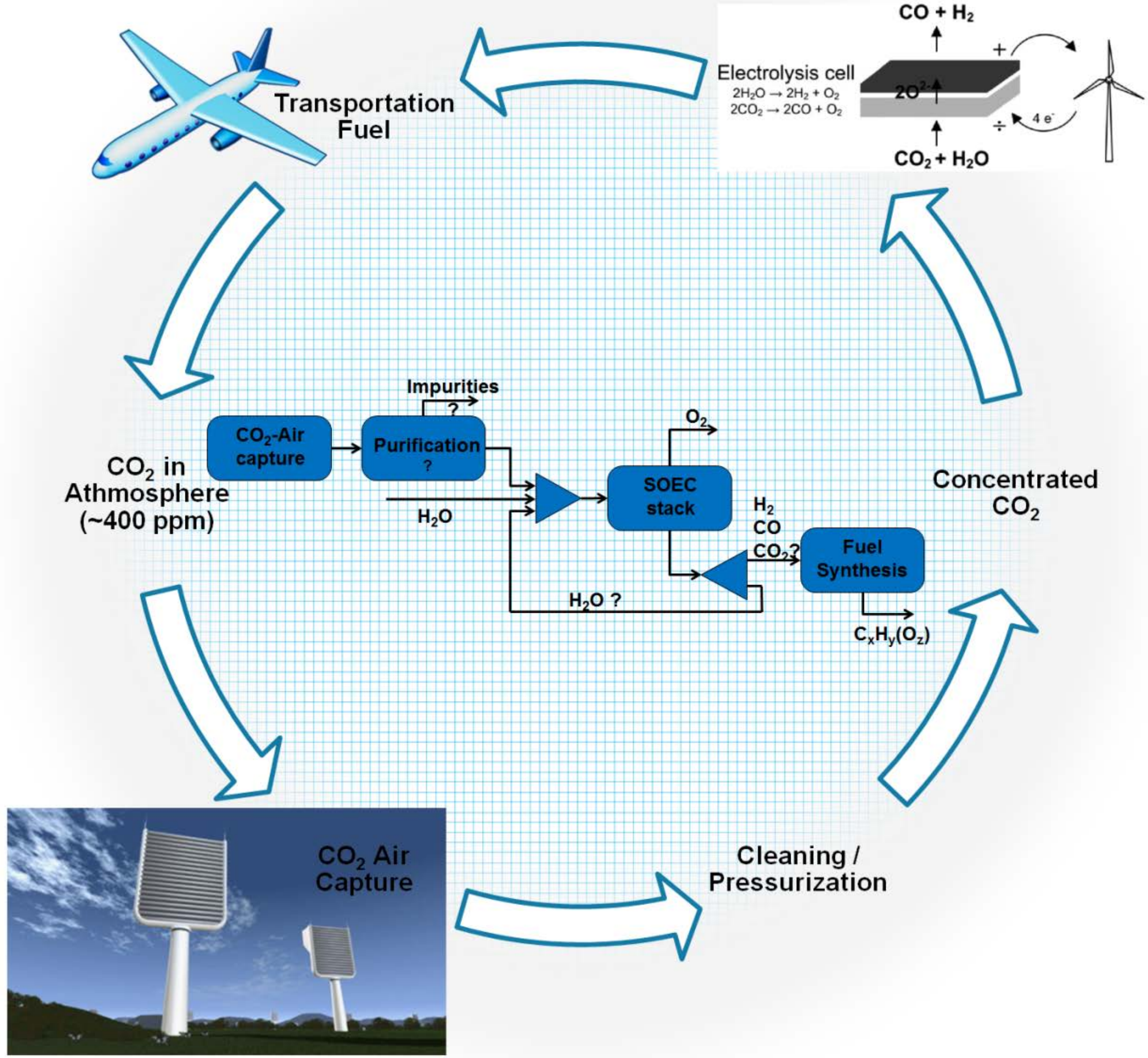
1. **Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).**

2. **Large SOEC systems - produce DME, gasoline and diesel - Iceland, Canada, Greenland, Argentina, Australia … geothermal, hydro, solar and wind.**

3. **Target market: replacement of natural gas and <u>liquid fuels for transportation</u>**

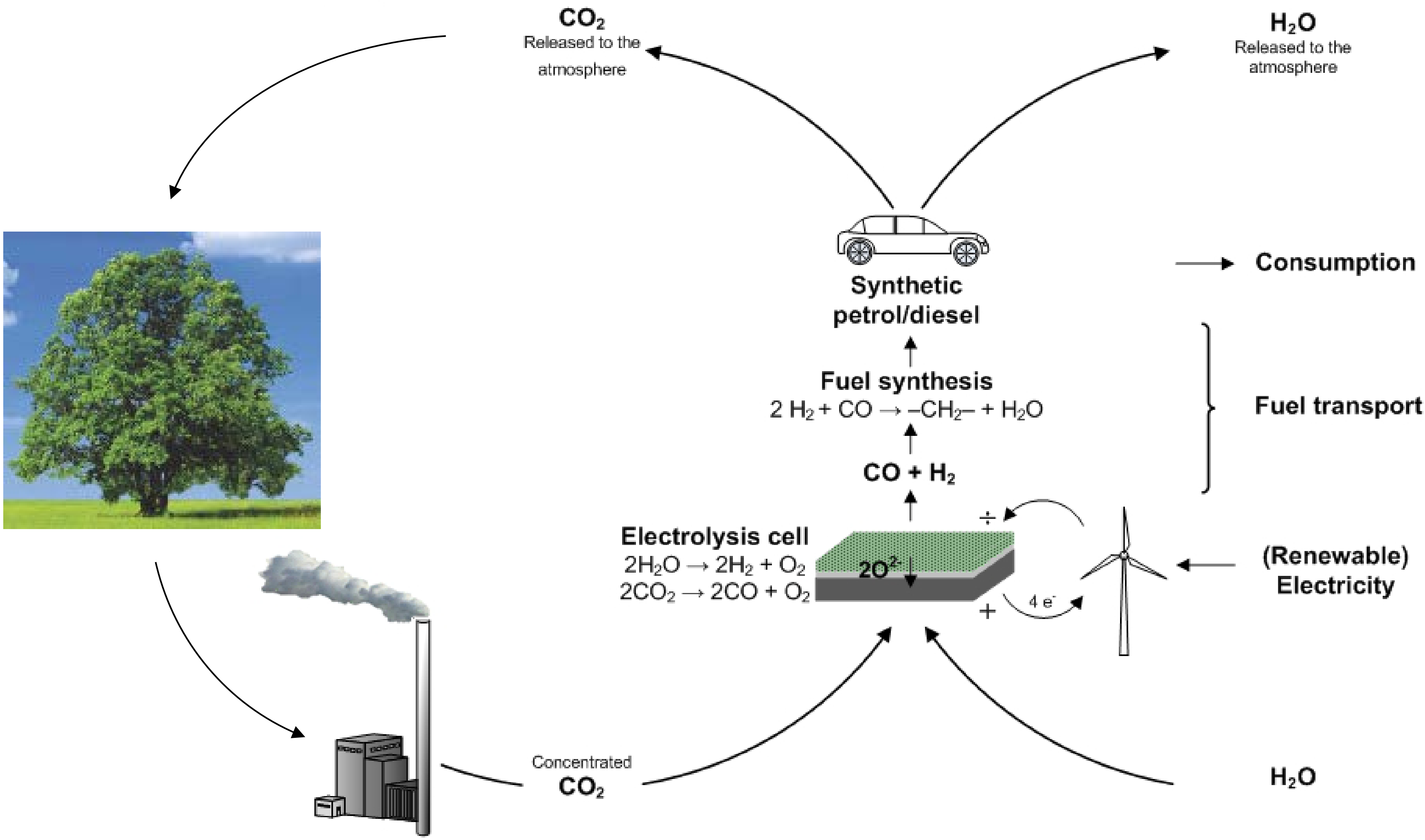
4. **All the infrastructure exists!!**

Vision, co-electrolysis for transport fuels

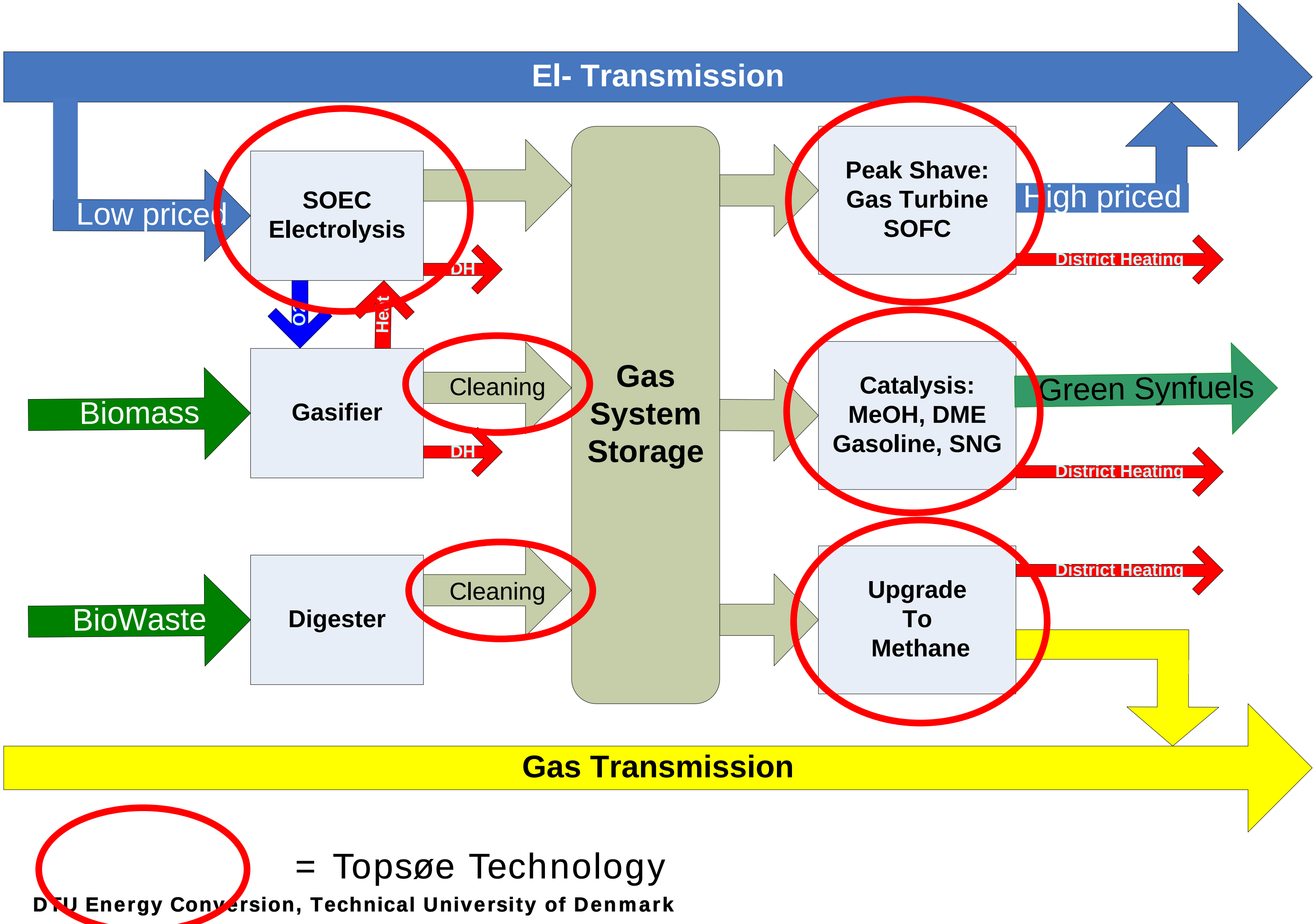


Vision, Biomass CO_2 recycling

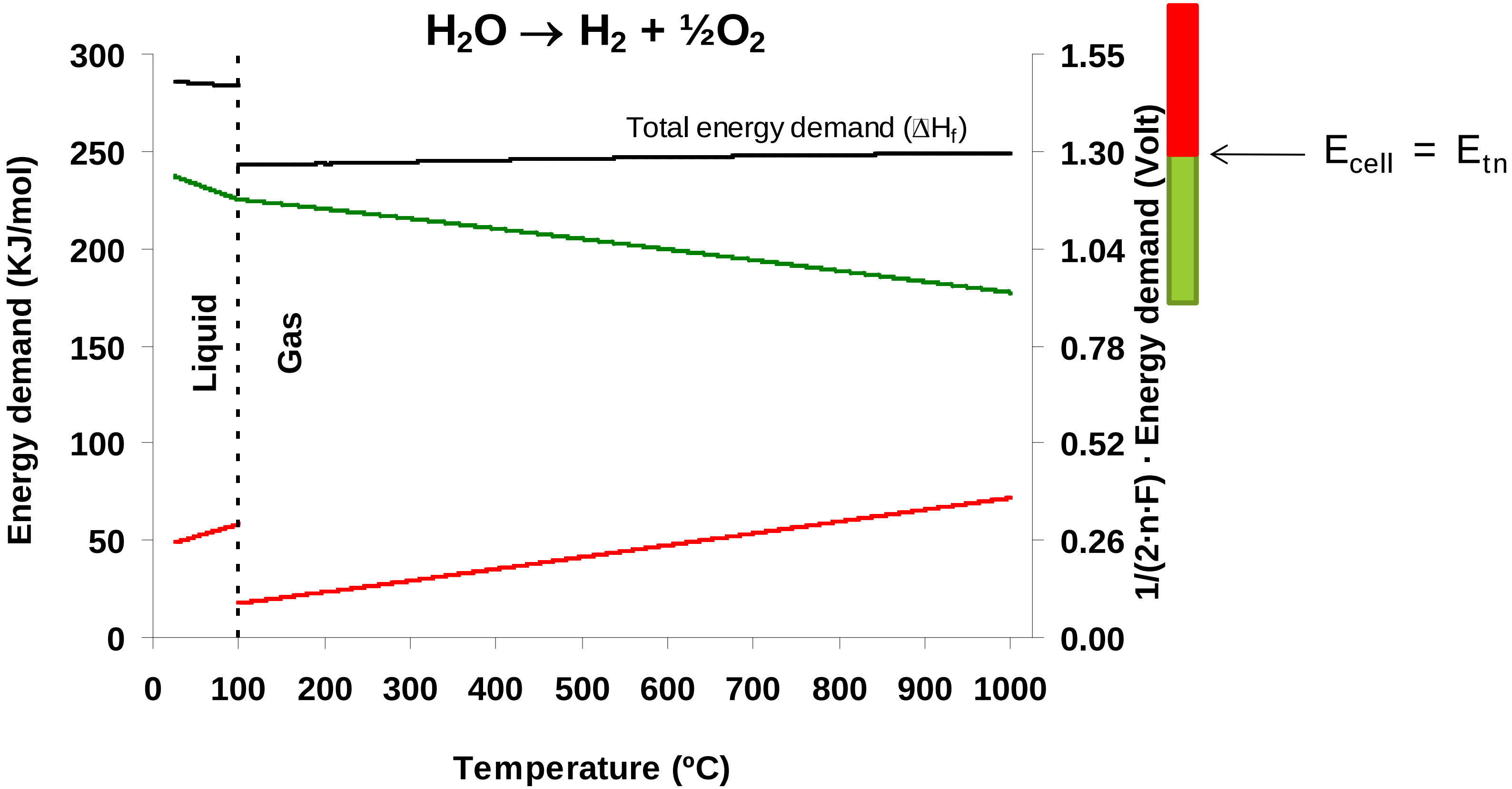
Short term realisation - CO_2 capture from industrial sources



Energinet.dk's vision for fossil fuel free Denmark in 2050 – The Wind Scenario



Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

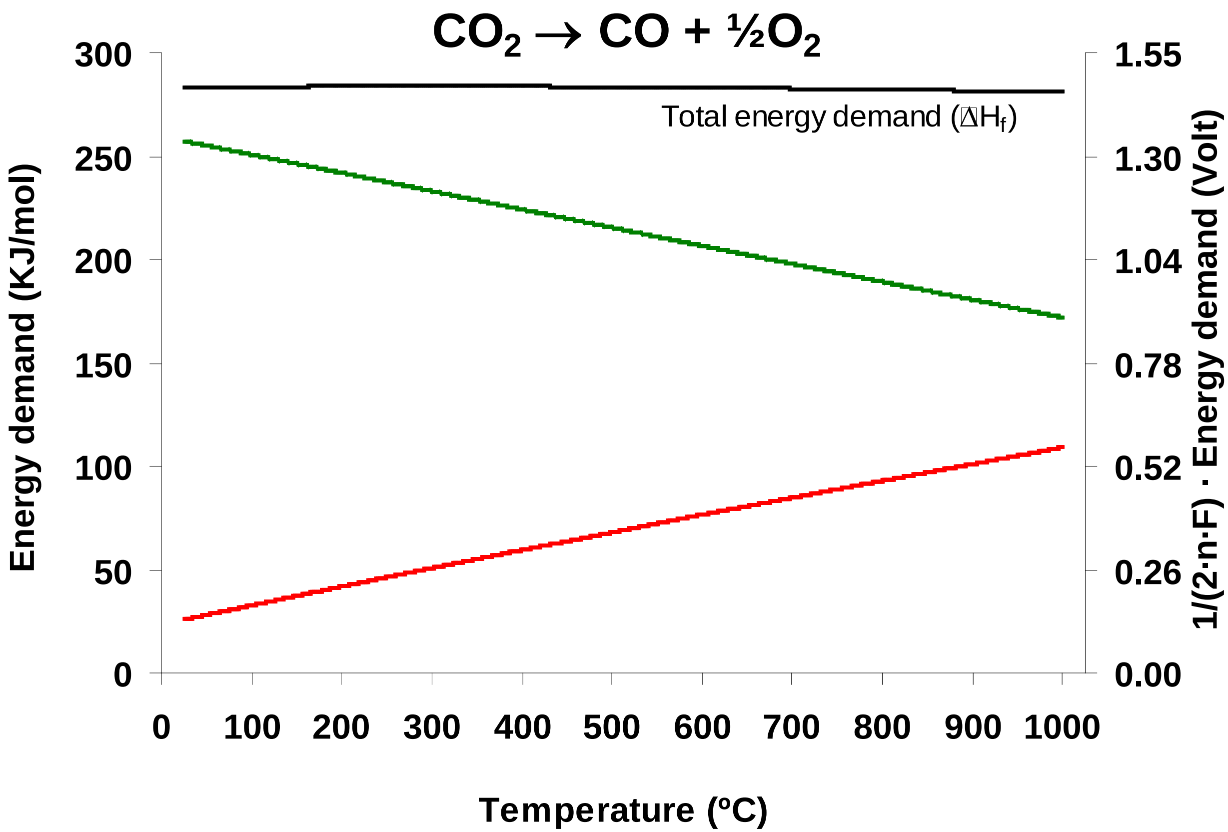
$i \propto E_{cell} - \Delta G/2F$

$E_{tn} = \Delta H/2F$

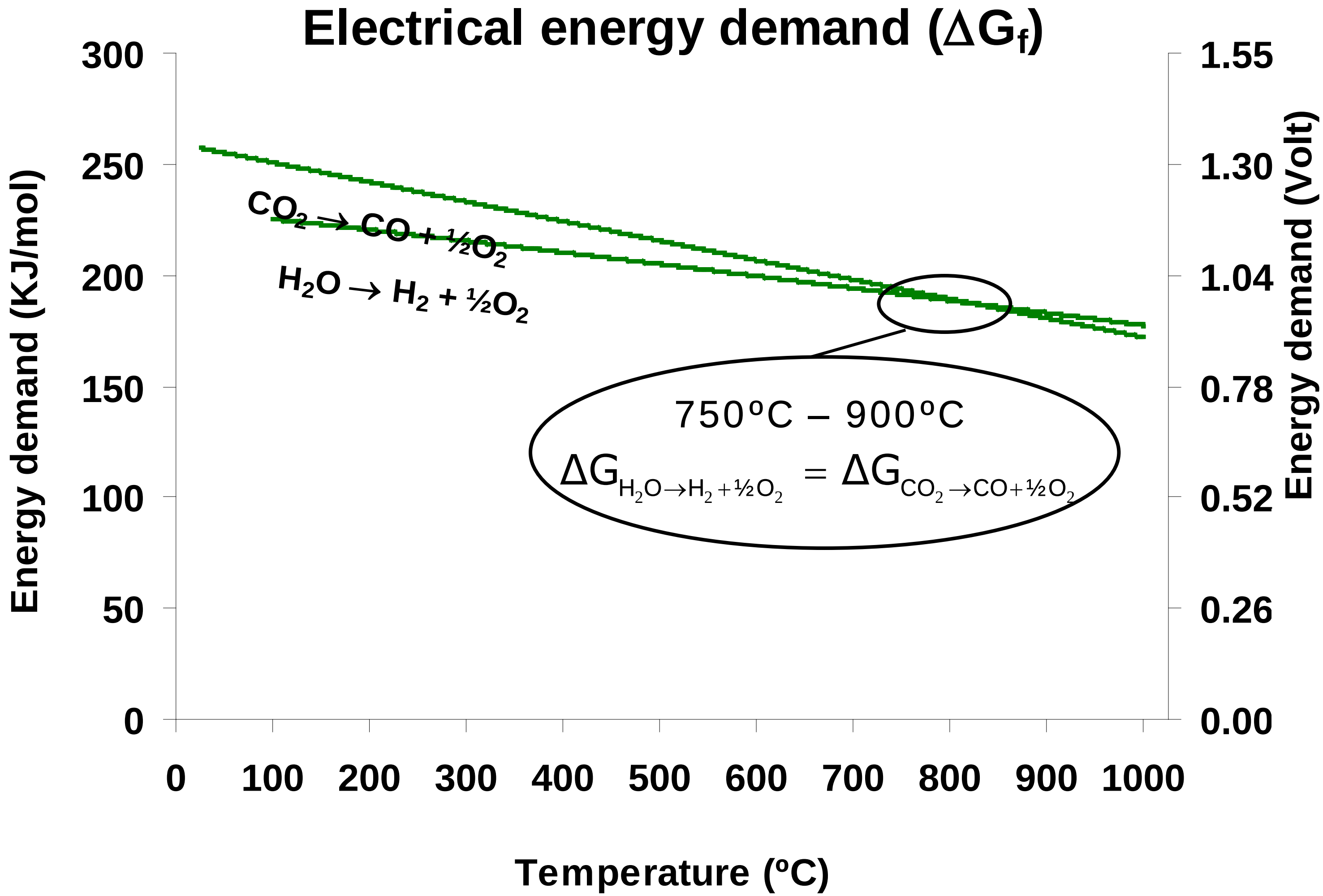
Price $\propto$ 1/i [A/cm^2] ,

$\Delta H/\Delta G > 1$, $\eta = 100\,\%$ at $E = E_{tn}$ (no heat loss)

Thermodynamics



Thermodynamics: CO_2 and H_2O



Electrolysis Cell Types

1. Simple aqueous electrolytes (e.g. KOH or K_2CO_3), room temperature to ca. 100 °C, 0.1 - 3 MPa pressure

2. Low temperature "solid" proton conductor membrane (PEM), 70 – 90 °C, and high temperature PEM 120 - 190 °C.

3. Immobilized aqueous K_2CO_3, Na_2CO_3 etc. in mesoporous structures – pressurized 200 – 300 °C, 0.3 – 10 MPa

4. Solid acids, 200 – 250 °C, pressurized?

5. Molten carbonate electrolytes, 800 – 950 °C, 0.1 Mpa

6. High temperature solid oxide ion conductor (stabilized zirconia), 650 – 950 °C, pressurized 0.5 – 5 MPa

Electrolyzer status

- Few types commercialized but - from an energy conversion and storage point of view - none of them are commercial in today's energy markets.
- The classical alkaline electrolyzer was commercialized during the first half of the 20th century.
- If significant amounts of synfuel via electrolysis in the very near future (the next 1 -5 years) – only alkaline electrolyzers is available on some scale.

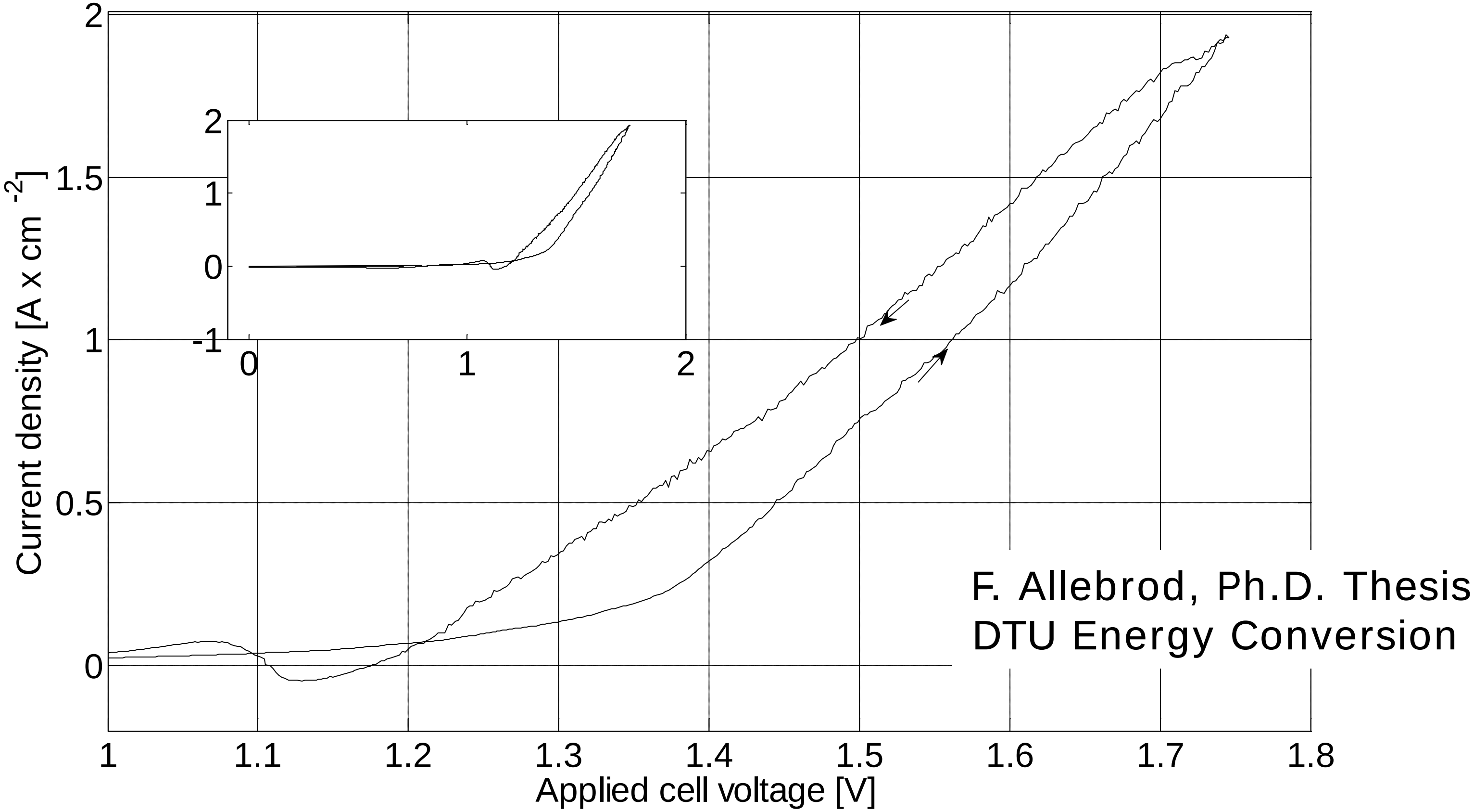
Other new 200 – 300 °C cell types

As part of the initiative called Catalysis for Sustainable Energy (CASE, www.case.dtu.dk) other types of electrolysis cells are being researched and developed at DTU.

- Solid Acids (CsH_2PO_4)
- Immobilized aqueous K_2CO_3
- Immobilized aqueous KOH

High Temperature and Pressure Alkaline (HT-AEC)

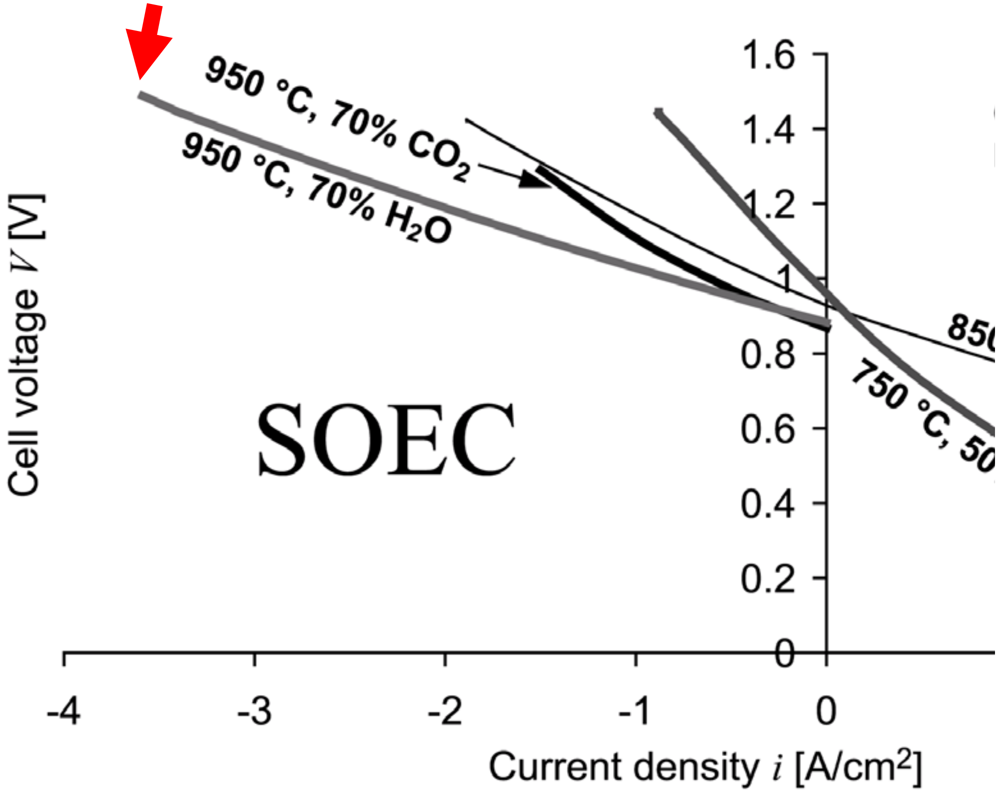
Conductivity of aqueous 45 wt% KOH immobilized in nano-porous structure reached 0.84 S·cm^{-1} at 200 ºC



Cyclic voltage sweep on a cell with nickel-based gas diffusion electrodes. Current densities of 1.0 A·cm^{-2} at 1.5V and 1.9 A·cm^{-2} at 1.75V. 3.7 MPa and 241 ºC. Calculated EMF 1.2 V. 1 cm^{2} button cell.

SOEC Cell performance

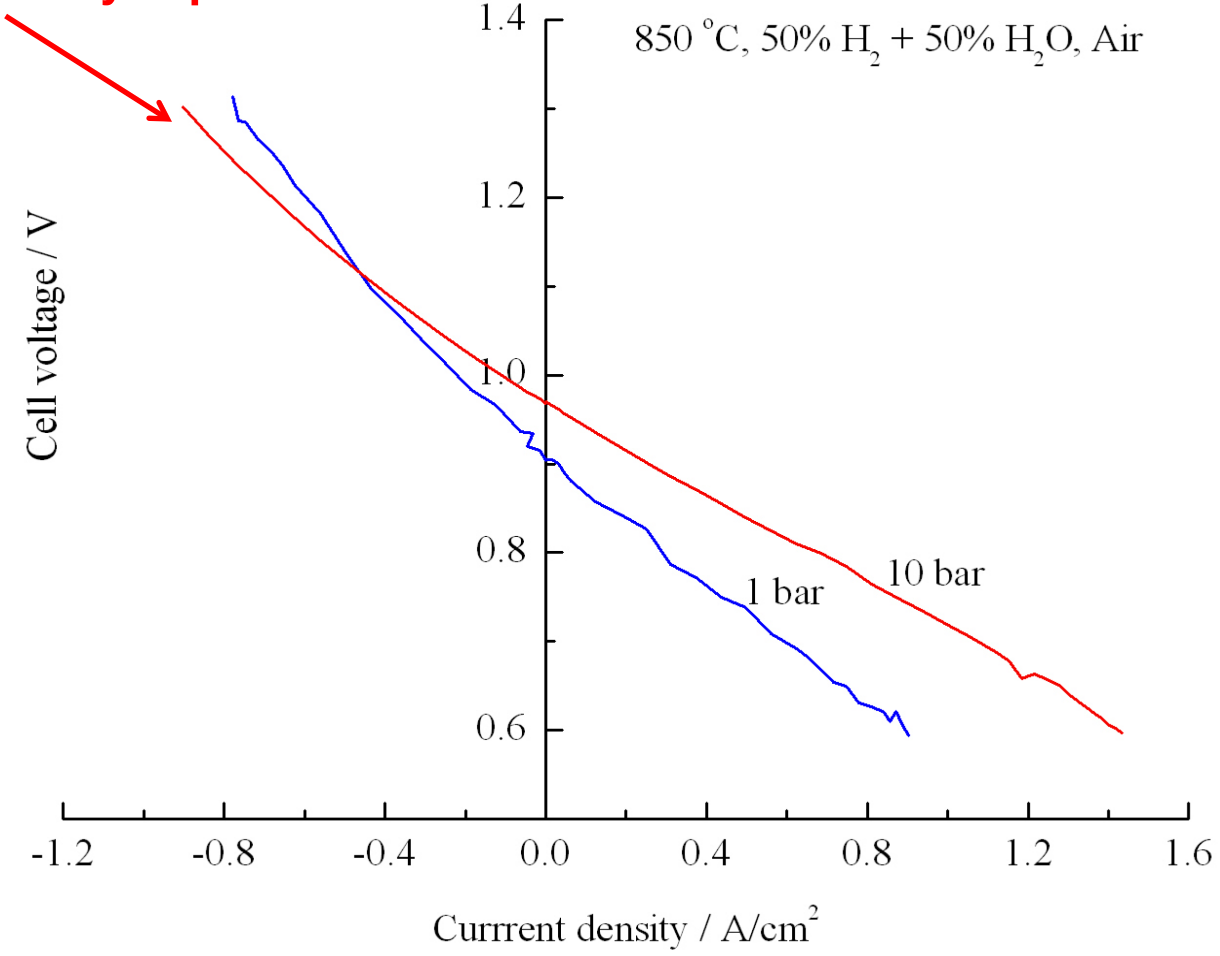
World record !



i - V **curves for a Ni-YSZ-supported Ni / YSZ / LSM SOC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO.** S.H. Jensen et al., International Journal of Hydrogen Energy, 32 (2007) 3253

SOEC Effect of pressure

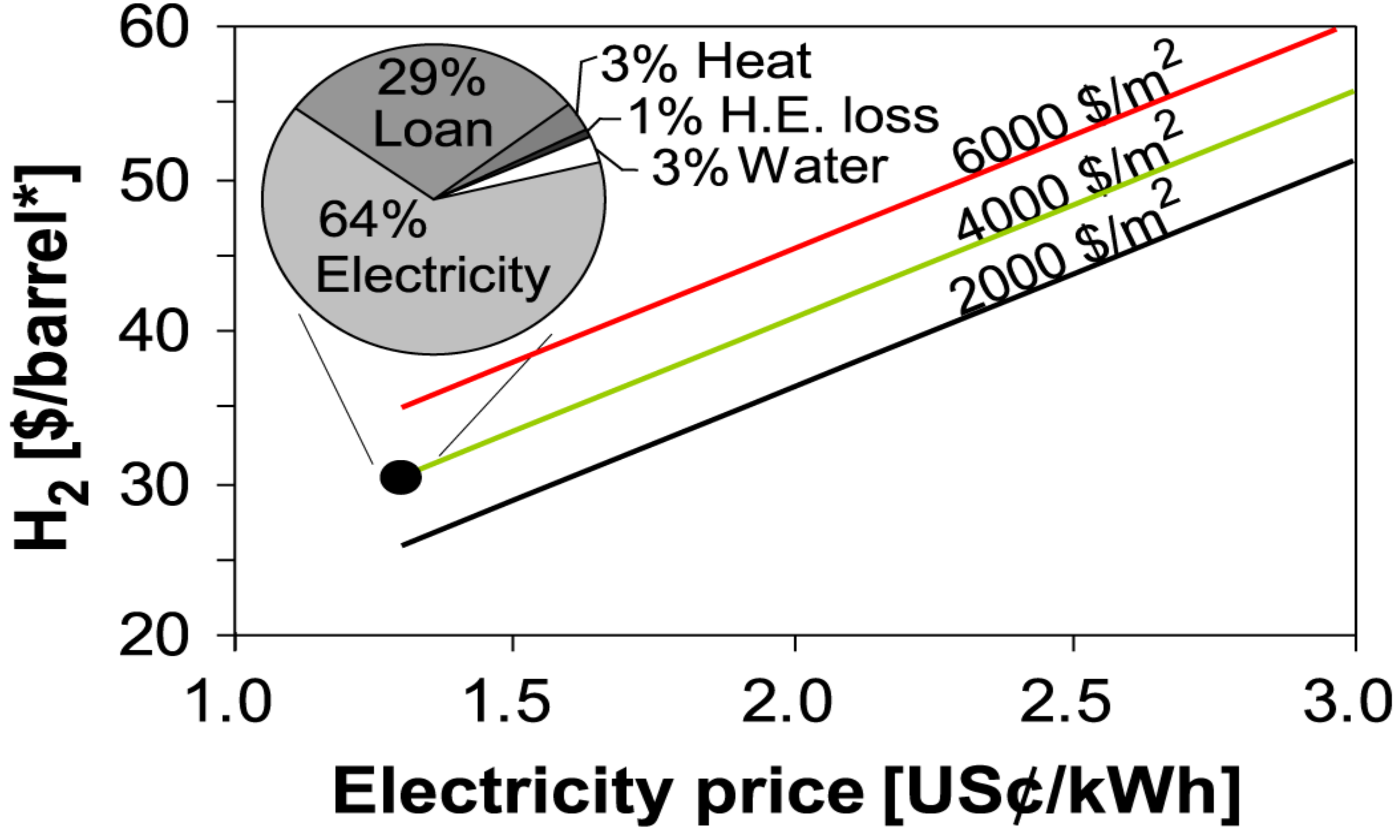
We get pressurized hydrogen with lower electricity input!



Economy assumptions for H_2 production using SOEC

Electricity	1.3US¢/kWh
Heat	0.3US¢/kWh
Investment	4000 $/m^2$ cell area
Demineralised Water	2.3 $/m^3$
Cell temperature	850 ° C
Heat reservoir temperature	110 °C
Pressure	1 atm
Cell voltage	1.29 V (thermo neutral potential)
Life time	10 years.
Operating activity	50%
Interest rate	5%
Energy loss in heat exchanger	5%
H_2O inlet concentration	95% (5% H_2)
H_2O outlet concentration	5% (95% H_2)

H_2 production – economy estimation

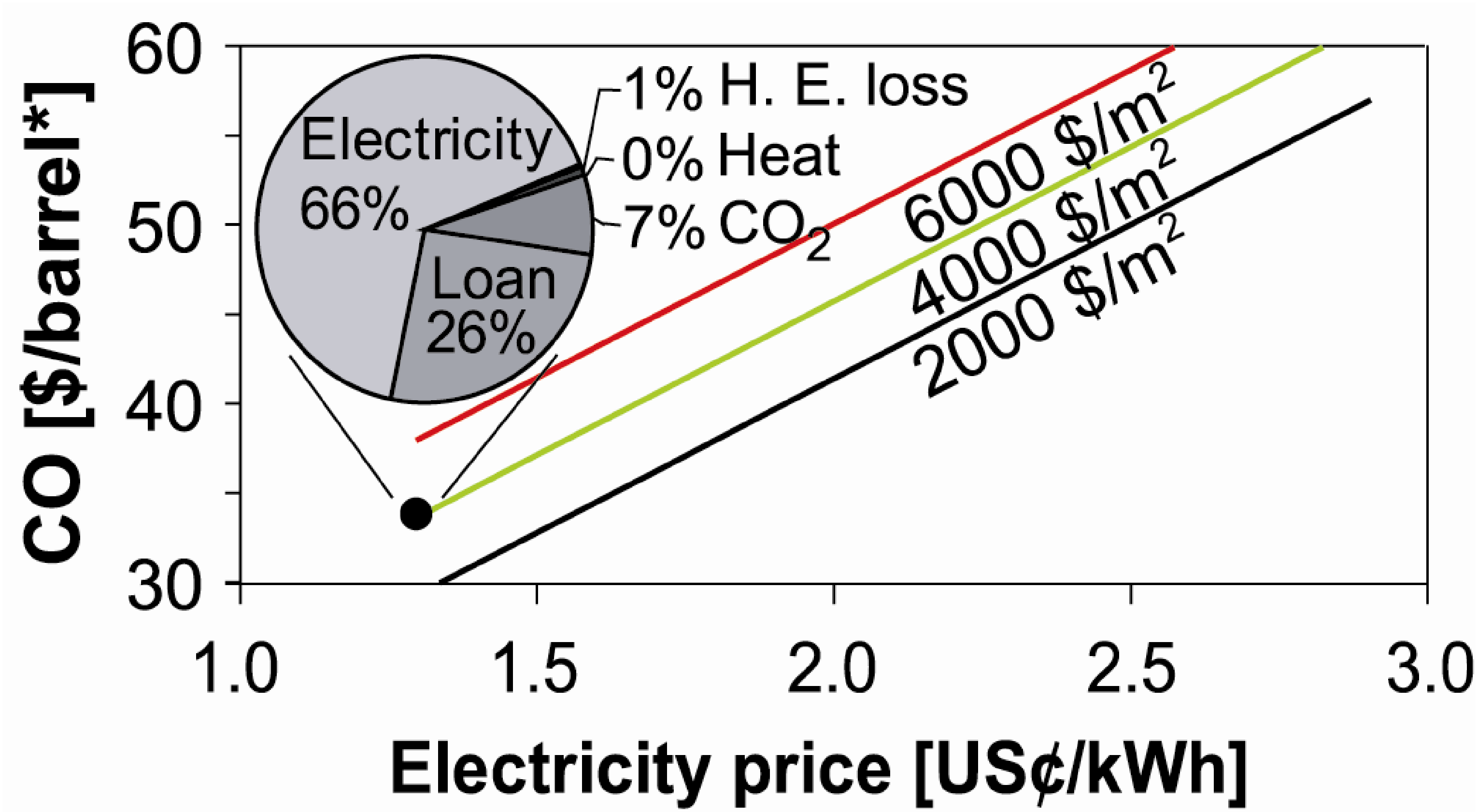


* Conversion of H_2 to equivalent crude oil price is on a pure energy content (J/kg) basis

Economy assumptions for CO production by SOEC

Electricity	1.3US¢/kWh
Heat	0.3US¢/kWh
Investment	4000 $/m^2$ cell area
CO_2	2.3 $/ton
Cell temperature	850 ° C
Heat reservoir temperature	110 °C
Pressure	1 atm
Cell voltage*	1.47 V (thermo neutral potential)
Life time	10 years.
Operating activity	50%
Interest rate	5%
Energy loss in heat exchanger	5%
CO_2 inlet concentration	95% (5% CO)
CO_2 outlet concentration	5% (95% CO)

CO production – economy estimation



* Conversion of CO to equivalent crude oil price is on a pure energy content (J/kg) basis

Concluding Remarks

- In order to fulfill the visions we need to produce at least H_2 by electrolysis and possibly CO
- We need to capture and purify CO_2 from suitable sources
- Both above point may technically be done by several technologies – but the economy is yet problematic for all of them
- Competition with shale gas and open pit coal mining will be very difficult in a free market
- Economic incentive has to be made by political means

Acknowledgements

I acknowledge support from our sponsors

- Danish Energy Authority
- Energinet.dk
- EU
- Topsoe Fuel Cell A/S
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
- The work of <u>many</u> colleagues over the years